**Carboranes as model hypercarbon systems; structural and bonding patterns in selected isoelectronic *closo* borane and carborane systems; $[B_nH_n]^{2-}$, $[1\text{-}CB_{n-1}H_n]^-$ and 1,n-$C_2B_{n-2}H_n$ (n = 5, 6, 7, 10 or 12)**

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***Dedicated on the occasion of his 75th birthday to Professor Tom Fehlner, good friend, pioneering chemist, and long-time research partner of KW.***

## SUMMARY

Computations have been carried out on the title boranes and carboranes, model hypercarbon cluster systems chosen to explore how effectively an individual carbon atom, whilst bonding by a normal 2-electron 2-centre bond to an *exo*-hydrogen atom, can also bond to sets of three, four or five equivalent boron atoms within a series of carborane clusters which have carbon atoms in axial sites of $C_{3v}$, $C_{4v}$ or $C_{5v}$ local symmetry. The calculated interatomic distances and bond orders and CH and BH group charges are reported, and the manner in which the introduction of CH units to replace $BH^-$ units in *closo* borane cages perturbs the distribution of the skeletal electrons in these clusters is discussed.

## INTRODUCTION

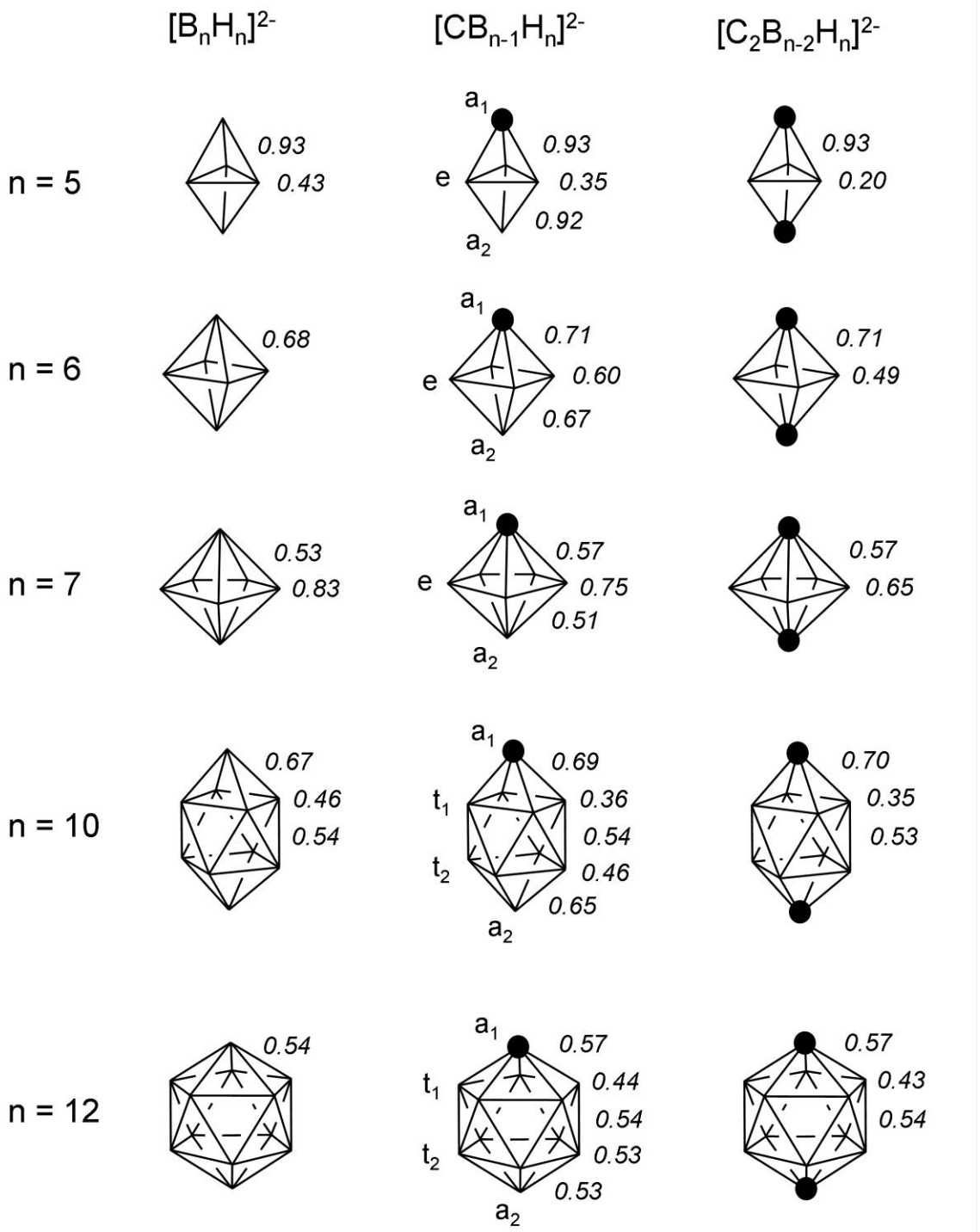
The deltahedral (or deltahedral fragment) shapes of borane and carborane clusters, and the way those shapes reflect formula types and skeletal electron numbers, have long been familiar.[1-16] Less familiar is how these skeletal electrons are distributed around the vertices, edges or faces of the deltahedra, though many calculations have been carried out to establish relative stabilities, probing group charges and showing the importance of skeletal connectivities.[17-23] Limited insight is provided by resonating localized 2-center 2-electron (2c2e) and 3-center 2-electron (3c2e) bond networks.[24,25] As carboranes can act as model hypercarbon systems to show how a carbon atom can form a single 2c2e bond to one (*exo*) atom whilst linked by fractional order bonds to three, four or five other atoms, it seemed profitable to explore and illustrate this by MP2/6-31G* calculations on a selected series of isoelectronic *closo* borane dianions $[B_nH_n]^{2-}$, monocarba-borane mono-anions $[1\text{-}CB_{n-1}H_n]^-$ and neutral dicarba-boranes 1,n-$C_2B_{n-2}H_n$, in order to explore how the distribution of the skeletal electrons over their pseudo-spherical cluster surfaces varies with the skeletal connectivities and nuclear charges of the cluster atoms.

The two sets of systems we chose to study, shown in Figure 1, were:-

(i) bipyramidal systems with n = 5, 6 or 7 skeletal atoms, in which two axial boron or carbon atoms occupy capping sites above and below an equatorial belt of 3, 4 or 5 boron atoms, and

(ii) bicapped antiprismatic systems with n =10 or 12 skeletal atoms, in which two boron or carbon atoms occupy the capping sites, above and below the staggered tropical belts of 4 or 5 boron atoms.

**Figure 1**. Each naked vertex represents BH and each black dot represents a CH vertex. Bond order values are shown in italics.




We deliberately selected the carborane isomers in which the carbon atoms occupied axial sites (a), rather than the equatorial (e) or tropical (t) sites that in certain cases are thermodynamically preferred, in order to place the carbon atoms in sites with as highly symmetrical environments as possible ($C_{3v}$, $C_{4v}$ or $C_{5v}$). In the first set of bipyramidal

systems, one can probe the effect of replacing one and then both of their axial anionic $[BH]^-$ units by (neutral) CH units above and below an equatorial belt of three, four or five boron atoms; in these carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$ and 1,7-$C_2B_5H_7$, the axial CH units compete with each other for electronic charge to bond to the same equatorial $B_3H_3$, $B_4H_4$ or $B_5H_5$ ring of atoms. In the second set, of bicapped antiprismatic systems 1,10-$C_2B_8H_{10}$ and 1,12-$C_2B_{10}H_{12}$, one can study how effectively the axial CH units bond to similar but distinct tropical $B_4H_4$ or $B_5H_5$ rings, each of which backs on to (and is staggered with respect to) another such tropical ring (with which it effectively shares an aromatic sextet of electrons).

## RESULTS AND DISCUSSION

### The calculational method

As we wished to consider series of compounds that included hypothetical unknown species as well as systems that have been prepared and well characterised analytically, spectroscopically, structurally and computationally, and wanted to explore variations in structural and bonding characteristics across series, we used MP2/6-31G* calculations throughout to monitor such variations which were likely to have been distorted if we had used a mix of experimental and computed data. MP2/6-31G* calculations have been shown by many studies of boranes and carboranes to afford optimised structures with interatomic distances of comparable precision to experimentally determined structures.[26] Indeed, such calculations are being increasingly used in borane and carborane chemistry to predict the structures and stabilities of ever more exotic systems, and routes thereto.[17-27]

We carried out MP2/6-31G* calculations on the fifteen systems $[B_nH_n]^{2-}$, $[1\text{-}CB_{n-1}H_n]^-$ and 1,n-$C_2B_{n-2}H_n$ (n = 5, 6, 7, 10, and 12) with the Gaussian09 computational package.[28] Our bond orders/indices were calculated by the Wiberg Bond Index method and the atomic and group charges by Natural Population Analysis (NPA) using the NBO 3.1 program within Gaussian09. These afforded the optimised geometries with the B-B and B-C bond distances and indices and atomic charges listed in Tables 1-5. Frequency calculations for all optimised geometries with symmetry constraints at MP2/6-31G* including the unfavorable high-energy isomers, $[1\text{-}CB_6H_7]^-$ and 1,7-$C_2B_5H_7$, showed no imaginary frequencies. Each triad of three isoelectronic species is considered in turn below.

### The trigonal bipyramidal species $[B_5H_5]^{2-}$, $[1\text{-}CB_4H_5]^-$ and 1,5-$C_2B_3H_5$

Bond lengths and indices, total bond indices at particular atoms, and CH and BH group charges for these systems are listed in Table 1. The parent dianion $[B_5H_5]^{2-}$, though as yet unknown, has been the subject of earlier calculations [3,19,20,29] which have shown the bonding between the axial and equatorial boron atoms to be far stronger than that between the equatorial atoms, as revealed again here, reinforcing the simplistic picture given by a localized bond description in which three 2c2e BB bonds along axial-

equatorial edges in one hemisphere, and three 3c2e BBB bonds in adjacent faces in the other hemisphere, but resonating between the two hemispheres, imply bond orders of 0.833′ and 0.333′ for the axial-equatorial and equatorial-equatorial bonds respectively.[13,30] A description of the bonding in terms of six axial-equatorial 2c2e bonds, and no bonding around the equator, with the equatorial boron atoms using only three AOs (one for the *exo* hydrogen, one each for the axial boron neighbours), can be ruled out.

**Table 1**. Calculated BB and BC bond distances and bond orders, and BH and CH group charges, for the trigonal bipyramidal *closo*-cluster systems $[B_5H_5]^{2-}$, $[1\text{-}CB_4H_5]^-$ and 1,5-$C_2B_3H_5$. Subscripts a and e identify axial and equatorial sites.

(a) Bond distances / pm (bond orders in parentheses)

| System | $C_{a_1}B_e$ | $B_eB_e$ | $B_{a_2}B_e$ |
|---|---|---|---|
| $[B_5H_5]^{2-}$ | - | 181 (0.43) | 167 (0.93) |
| $[1\text{-}CB_4H_5]^-$ | 155 (0.93) | 182 (0.35) | 167 (0.92) |
| 1,5-$C_2B_3H_5$ | 155 (0.93) | 184 (0.20) | - |

(b) Group charges (total order of skeletal bonds to that group)

| System | $C_{a_1}H$ | $B_eH$ | $B_{a_2}H$ |
|---|---|---|---|
| $[B_5H_5]^{2-}$ | - | -0.32 (2.72) | -0.53 (2.79) |
| $[1\text{-}CB_4H_5]^-$ | -0.66 (2.79) | +0.03 (2.54) | -0.42 (2.76) |
| 1,5-$C_2B_3H_5$ | -0.62 (2.79) | +0.41 (2.26) | - |

The effect of replacing one and then both of the axial boron atoms of $[B_5H_5]^{2-}$, formally as $B^-$ anions, by neutral carbon atoms, is reflected in the data in Table 1 for $[1\text{-}CB_4H_5]^-$ and 1,5-$C_2B_3H_5$.[31,32] The most marked bonding effect is on that between the equatorial boron atoms, which move only slightly further apart though the bond index between them decreases dramatically, from 0.43 to 0.35 then 0.20 as successive axial carbon atoms are introduced. The total skeletal bond indices of the equatorial set of boron atoms decrease in the same sequence from 2.72 to 2.54 to 2.26, markedly lower values than those (2.79, 2.76) of the axially-located boron atoms. No significant change occurs in the bond indices of the axial-equatorial bonds, which are essentially **the same** for BC bonds as BB bonds.

Drainage of electronic charge from the equatorial BH units as axial CH units are introduced is reflected in the stepwise change in the charge on each equatorial BH unit from –0.32 to +0.03 to +0.41 a.u.. The equatorial $B_3H_3$ ring in $[B_5H_5]^{2-}$ bears a formal negative charge of –0.96; this changes dramatically to +0.09 in $[CB_4H_5]^-$, becoming +1.23 a.u. in $C_2B_3H_5$, as axial BH units, each bearing charges of –0.53 a.u. in the dianion, are replaced by CH units each bearing charges of –0.62 a.u. in the neutral carborane $C_2B_3H_5$.

**The octahedral species $[B_6H_6]^{2-}$, $[1\text{-}CB_5H_6]^-$ and 1,6-$C_2B_4H_6$**

Bond lengths and indices, total skeletal bond indices at particular atoms, and CH and BH group charges for these systems are listed in Table 2. The parent dianion $[B_6H_6]^{2-}$ is of interest as one of the two most stable known[33,34] dianions $[B_nH_n]^{2-}$ (the other is $[B_{12}H_{12}]^{2-}$). Its octahedral symmetry requires a formal charge of –0.333′ a.u. to be associated with each BH unit, and a bond order of 7/12, i.e. 0.583′ for each skeletal BB link as seven skeletal bond pairs are spread over 12 BB links.

**Table 2**. Calculated data for the octahedral *closo*-cluster systems $[B_6H_6]^{2-}$, $[1\text{-}CB_5H_6]^-$ and $1,6\text{-}C_2B_4H_6$.

(a) Bond distances / pm (bond orders in parentheses)

| System | $C_{a_1}B_e$ | $B_eB_e$ | $B_{a_2}B_e$ |
|---|---|---|---|
| $[B_6H_6]^{2-}$ | - | 173 (0.68) | 173 (0.68) |
| $[1\text{-}CB_5H_6]^-$ | 162 (0.71) | 172 (0.60) | 173 (0.67) |
| $1,6\text{-}C_2B_4H_6$ | 162 (0.71) | 171 (0.49) | - |

(b) Group charges (total order of skeletal bonds to that group)

| System | $C_{a_1}H$ | $B_eH$ | $B_{a_2}H$ |
|---|---|---|---|
| $[B_6H_6]^{2-}$ | - | -0.33 (2.72) | -0.33 (2.72) |
| $[1\text{-}CB_5H_6]^-$ | -0.46 (2.84) | -0.08 (2.54) | -0.21 (2.68) |
| $1,6\text{-}C_2B_4H_6$ | -0.38 (2.84) | +0.19 (2.40) | - |

The calculated BH group charge of –0.33 does indeed confirm the expected value, though the calculated BB bond index of 0.68 significantly exceeds the expected value. As two opposed BH units in the dianion are replaced stepwise by CH units, in going from $[B_6H_6]^{2-}$ to $[1\text{-}CB_5H_6]^-$ and then $1,6\text{-}C_2B_4H_6$,[35,36] the bond distances between the equatorial boron atoms decrease slightly, as if bonding between these atoms was increasing. However, the equatorial bond indices are calculated to decrease from 0.68 to 0.60 to 0.49 over the series as the axial carbon atoms are introduced, and the total skeletal bond indices of the equatorial boron atoms fall from 2.72 to 2.54 to 2.40 in the same sequence. The decrease in the BB distances may result from the smaller size of the carbon atoms to which they become attached over this sequence.

Despite their high overall coordination numbers (5), the carbon atoms in the anion $[CB_5H_6]^-$ and in the neutral $C_2B_4H_6$ achieve total skeletal bond indices of 2.84. The axial-equatorial BC links have indices 0.71, marginally higher than those of the BB links they replace, and the charges on the individual equatorial BH units change from –0.33 to –0.08 to +0.19 a.u., implying that the overall charge on the equatorial belt of four BH units changes very substantially from –1.33 to –0.32 to +0.76 a.u. as the two CH units are introduced. These CH units bear charges of –0.38 a.u. in the neutral carborane $C_2B_4H_6$, less negative than their counterparts in $C_2B_3H_5$ as appropriate for CH units of higher connectivity.

**The pentagonal bipyramidal species $[B_7H_7]^{2-}$, $[1\text{-}CB_6H_7]^-$ and $1,7\text{-}C_2B_5H_7$**

Bond lengths and indices, total bond indices at particular atoms, and atomic charges for these systems are listed in Table 3. For the trigonal bipyramidal and octahedral species just considered, we were dealing with progressions from the parent dianion $[B_nH_n]^{2-}$ to the thermodynamically most stable neutral carborane $C_2B_{n-2}H_n$. However, in this pentagonal bipyramidal series we are considering progression from the parent borane dianion[37] $[B_7H_7]^{2-}$ (which had only recently been structurally characterised[38]) to the least thermodynamically stable dicarba-heptaborane, 1,7-$C_2B_5H_7$, in placing the carbon atoms in high-k (connectivity) sites, whereas their preference is for the low-k equatorial sites in which they are found in the known dicarba-heptaboranes.[39-41] Nevertheless the isomers in Table 3 are useful model systems with which to test the consequences of placing carbon atoms in high-connectivity sites.

**Table 3**. Calculated data for the pentagonal bipyramidal *closo*-systems $[B_7H_7]^{2-}$, [1-$CB_6H_7]^-$ and 1,7-$C_2B_5H_7$.

(a) Bond distances / pm (bond orders in parentheses)

| System | $C_{a_1}B_e$ | $B_eB_e$ | $B_{a_2}B_e$ |
|---|---|---|---|
| $[B_7H_7]^{2-}$ | - | 166 (0.83) | 182 (0.53) |
| [1-$CB_6H_7]^-$ | 173 (0.57) | 164 (0.75) | 182 (0.51) |
| 1,7-$C_2B_5H_7$ | 174 (0.57) | 163 (0.65) | - |

(b) Group charges (total order of skeletal bonds to that group)

| System | $C_{a_1}H$ | $B_eH$ | $B_{a_2}H$ |
|---|---|---|---|
| $[B_7H_7]^{2-}$ | - | -0.33 (2.72) | -0.17 (2.65) |
| [1-$CB_6H_7]^-$ | -0.37 (2.85) | -0.12 (2.52) | -0.03 (2.55) |
| 1,7-$C_2B_5H_7$ | -0.25 (2.85) | +0.10 (2.44) | - |

Again, there is a decrease in calculated equatorial BB distances as CH units are introduced, though this should not be taken as indicating stronger bonding around the equator. If such substitutions could be achieved experimentally, we calculate that the bond indices of the equatorial BB bonds would decrease as axial CH units replace BH units, from 0.83 to 0.75 to 0.65, and the charge on each equatorial BH unit would swing from –0.33 to –0.12 to +0.10 a.u., i.e. the charge on the equatorial $B_5H_5$ ring would change stepwise from –1.65 to –0.60 to +0.50 a.u.. The total skeletal bond indices of the equatorial boron atoms would fall from 2.72 to 2.52 to 2.44 as the axial carbon atoms were introduced. Each of the CH units in 1,7-$C_2B_5H_7$ would bear a negative charge of –0.25 a.u., less again than that in $C_2B_3H_5$ and $C_2B_4H_6$, though the total bond indices of their carbon atoms (2.85) would be higher than those in the smaller carboranes. The bond indices of the B-C axial-equatorial bonds (0.57) would be marginally higher than those of the axial-equatorial B-B bonds they replace (0.53, 0.51).

**General patterns for these bipyramidal species with 5, 6 or 7 skeletal atoms**

Before extending our discussion to the 10- and 12-atom species which have bicapped antiprismatic structures, it is helpful to consider general trends within the bipyramidal systems. We have focussed primarily in our discussion so far on the way that the bonding

and electron density around the equatorial sets of boron atoms decreases when CH units replace BH units in the axial sites above and below the equatorial sets of BH units. It is worth noting now how the bonding between adjacent equatorial atoms, and between axial and equatorial atoms, changes very significantly with the cluster size in the homonuclear series of borane dianions $[B_5H_5]^{2-}$, $[B_6H_6]^{2-}$ and $[B_7H_7]^{2-}$. These three *closo*-borane dianions may be regarded as derived from intrinsically unstable *arachno*- planar $[B_3H_3]^{6-}$, $[B_4H_4]^{6-}$ and $[B_5H_5]^{6-}$ systems stabilised by axial $[BH]^{2+}$ units located above and below their ring planes (Fig. 2). The *arachno* equatorial ring systems themselves are formally aromatic ring systems that are however unstable because they contain too many electrons to be accommodated in truly bonding orbitals.

In $[B_3H_3]^{6-}$, for example, only two of the pi-electrons could be accommodated in a pi-bonding MO; the remaining two pairs of pi electrons would have to occupy pi-antibonding MOs. In $[B_4H_4]^{6-}$, a formally aromatic (six pi-electron) ring system contains enough electrons not only for a bond pair for each of their B-B sigma bonds but also three further pairs of electrons that have to be accommodated in the ring pi-system, with two of these pi- electron pairs at best non-bonding. Only in the case of $[B_5H_5]^{6-}$ might the last two pairs of pi-electrons be accommodated in weakly pi-bonding MOs. However, when $BH^{2+}$ units are available to cap these unstable aromatic ring systems in axial sites above and below the rings, as in the *closo*-boranes $[B_nH_n]^{2-}$ (n = 5, 6 or 7), they reduce the destabilising negative charge and give a bonding role, between axial and equatorial atoms, to the surplus pi-electrons. In bonding to the equatorial rings, the axial $[BH]^{2+}$ units soak up the surplus pi-electron density, and indeed some of the sigma-bonding electron density, from the equatorial ring systems into their three vacant orbitals.

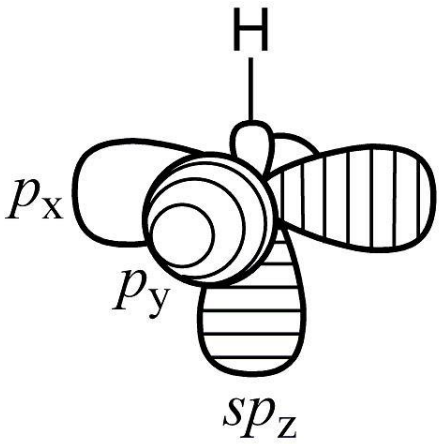



**Figure 2a**. The three empty orbitals available for skeletal bonding on a $[BH]^{2+}$ or $[CH]^{3+}$ unit.

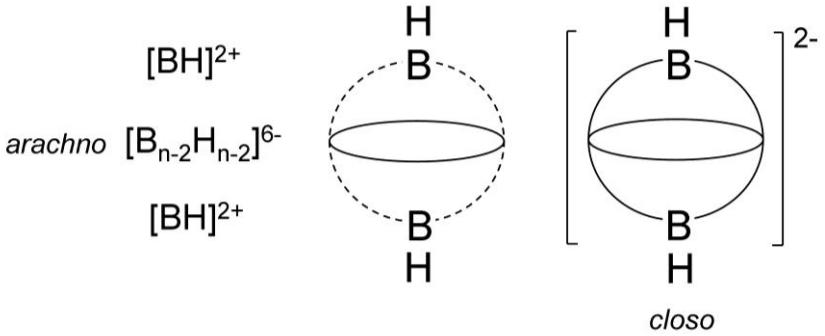



**Figure 2b**. The bipyramidal systems regarded as built up from *arachno*-$[B_{n-2}H_{n-2}]^{6-}$ six pi-electron ring systems capped above and below by $BH^{2+}$ or $CH^{3+}$ units.

Progressing along the series $[B_5H_5]^{2-}$, $[B_6H_6]^{2-}$, $[B_7H_7]^{2-}$, one can see, from the equatorial B-B bond indices in Tables 1, 2 and 3, how much more of the ring electron density is retained for bonding between the ring atoms as their number increases, both in the parent *closo*- boranes $[B_nH_n]^{2-}$ and in the carborane anions $[CB_{(n-1)}H_n]^-$ and neutral carboranes $C_2B_{(n-2)}H_n$, even though the bond order of the equatorial BB bonds decreases as axial CH units replace axial BH units.

**The bicapped antiprismatic systems related to $[B_{10}H_{10}]^{2-}$ and $[B_{12}H_{12}]^{2-}$**

Before considering these larger clusters individually, it is worth noting briefly how they resemble or differ from the bipyramidal systems we have just discussed. Though the sites occupied by the axial BH or CH units in the bicapped antiprismatic systems, over $B_4H_4$ squares or $B_5H_5$ pentagons, resemble the sites in the 6- or 7-atom *closo* species already considered, the central cores of the bicapped antiprismatic systems consist of formally *arachno* 8- or 10-atom antiprismatic $[B_8H_8]^{6-}$ or $[B_{10}H_{10}]^{6-}$ units made up of pairs of 4- or 5-atom rings in staggered arrays. These in turn may be regarded as built from individual $[B_4H_4]^{6-}$ or $[B_5H_5]^{6-}$ units brought together in staggered arrays, when three pairs of electrons from their separate pi-systems are discarded as no longer needed. The antiprismatic *arachno* species effectively share a common set of six pi-electrons with which to bond to axial units in forming *closo*-species.

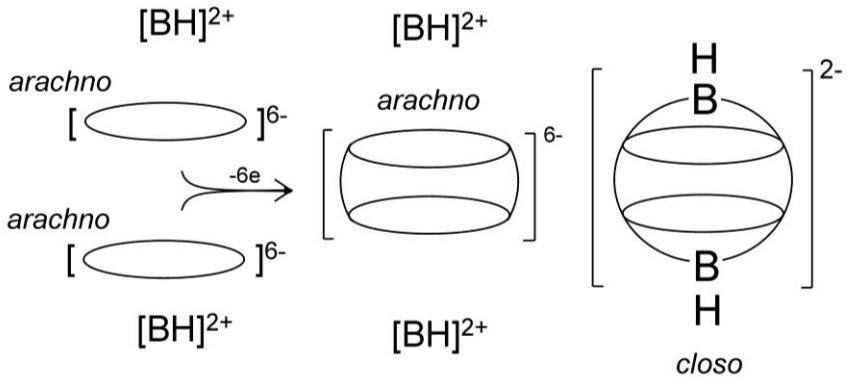


**Figure 3.** The bicapped antiprismatic clusters regarded as built up from separate axial and tropical components; Each axial $[BH]^{2+}$ or $[CH]^{3+}$ unit makes available three empty frontier orbitals to accommodate electronic charge from the $[B_{n-2}H_{n-2}]^{6-}$ six pi-electron arachno core of these antiprismatic systems.

### The bicapped square antiprismatic systems $[B_{10}H_{10}]^{2-}$, $[1\text{-}CB_9H_{10}]^{-}$ and $1,10\text{-}C_2B_8H_{10}$

Bond angles and indices, total bond indices at particular atoms, and atomic charges for these systems are listed in Table 4. These clusters resemble those with an octahedral arrangement of their skeletal atoms in that, in both sets, the axial atoms cap squares of boron atoms.[42-44] However, whereas in the octahedral systems, the capped boron atoms occupy equatorial sites, capped on both sides by axial atoms, in the square antiprismatic clusters the boron squares occupy tropical sites, with an axial capping atom on one side and another (staggered) set of tropical atoms on the other side separating the first tropical set of boron atoms from the second axial capping atom. Another point of difference between $[B_6H_6]^{2-}$ and $[B_{10}H_{10}]^{2-}$ is the lower overall electron density in the latter, which has 11 skeletal bond pairs spread over 10 BH units linked by 24 edges, whereas the former has 7 skeletal pairs spread over 6 BH units linked by 12 edges.

**Table 4**. Calculated data for the bicapped tetragonal antiprismatic *closo*-cluster systems $[B_{10}H_{10}]^{2-}$, $[1\text{-}CB_9H_{10}]^{-}$ and $1,10\text{-}C_2B_8H_{10}$. Subscripts a and t identify axial and tropical sites, numbered to indicate the hemisphere.

(a) Bond distances / pm (bond orders in parentheses)

| System | $C_{a_1}B_{t_1}$ | $B_{t_1}B_{t_1}$ | $B_{t_1}B_{t_2}$ | $B_{t_2}B_{t_2}$ | $B_{a_2}B_{t_2}$ |
|---|---|---|---|---|---|
| $[B_{10}H_{10}]^{2-}$ | - | 183 (0.46) | 181 (0.54) | 183 (0.46) | 170 (0.67) |
| $[1\text{-}CB_9H_{10}]^{-}$ | 160 (0.69) | 184 (0.36) | 180 (0.54) | 184 (0.46) | 170 (0.65) |
| $1,10\text{-}C_2B_8H_{10}$ | 160 (0.70) | 184 (0.35) | 181 (0.53) | 184 (0.35) | - |

(b) Group charges (total order of skeletal bonds to that group)

| System | $C_{a_1}H$ | $B_{t_1}H$ | $B_{t_2}H$ | $B_{a_2}H$ |
|---|---|---|---|---|
| $[B_{10}H_{10}]^{2-}$ | - | -0.18 (2.67) | -0.18 (2.67) | -0.27 (2.68) |
| $[1\text{-}CB_9H_{10}]^{-}$ | -0.53 (2.76) | +0.08 (2.49) | -0.16 (2.65) | -0.13 (2.60) |
| $1,10\text{-}C_2B_8H_{10}$ | -0.45 (2.80) | +0.11 (2.46) | +0.11 (2.46) | - |

Despite the similar geometry of the BH environments in these two systems, the calculated bonding environment at the capping atoms in $[B_{10}H_{10}]^{2-}$ differs from that of all of the BH units in $[B_6H_6]^{2-}$ in that the overall charge on the capping (axial) BH unit in $[B_{10}H_{10}]^{2-}$, at –0.27 a.u., is some 20% lower than that (-0.33 a.u.) on its counterpart in $[B_6H_6]^{2-}$. However, the tropical BH units in $[B_{10}H_{10}]^{2-}$ suffer a significant reduction in electronic charge compared with their equatorial counterparts in $[B_6H_6]^{2-}$, bearing a charge of only 0.18 a.u., as the electronic charge they shared in the octahedral system must now be spread over the links to the other set of tropical atoms. Interestingly, these links, between one set of tropical atoms and the other, have bond orders (0.54) higher than those between atoms within the same tropical set (0.46).

When one and then two axial CH units are introduced to replace the axial $BH^-$ units in $[B_{10}H_{10}]^{2-}$, the effect already noted in the bipyramidal systems is evident. The overall negative charge is reduced by one unit for each carbon atom introduced, and the negative charge acquired by the CH units exceeds significantly the negative charge of the axial BH units displaced. Tropical rings of BH units, which carry charges of -0.72 a u in the parent borane dianion, become positively charged when the adjacent boron atom is replaced by carbon, and the bonding between the boron atoms within a capped tropic decreases in bond order to a value only two-thirds of that between atoms in different tropics, though the lengths of the tropical BB bond show negligible sensitivity to whether axial BH or CH units cap that tropic.

**The icosahedral (bicapped pentagonal antiprismatic) systems $[B_{12}H_{12}]^{2-}$, $[1\text{-}CB_{11}H_{12}]^-$ and 1,12-$C_2B_{10}H_{12}$**

These icosahedral systems provide the frameworks for the most important family of borane/carborane clusters. The icosahedral structure and stability of the dianion $[B_{12}H_{12}]^{2-}$ was predicted by Longuet-Higgins and Roberts[45] before it was first prepared[34] and structurally characterised.[46] The anion $[CB_{11}H_{12}]^-$ is the parent species from which many derivatives have been prepared in the search for large weakly coordinating anions [47] for use in the synthesis of novel cations, including hypercoordinate carbocations.[48] The neutral icosahedral carborane, 1,12-dicarbadodecaborane (*para*-carborane), is probably the most stable known carborane.[49] Many structural studies[1] have been carried out on the parent carboranes and assorted derivatives, confirming the skeletal geometries discussed here.

In the icosahedral dianion $[B_{12}H_{12}]^{2-}$, all of the BH units are equivalent and therefore each bears a charge of -0.166′. With thirteen skeletal electron pairs to allocate to thirty BB links, these are expected to have a bond order of 13/30, i.e. 0.433′. As was the case in the smaller *closo* boranes we have considered, the calculated bond order, 0.54, is somewhat higher than that expected from the total number of skeletal bonding electrons. Calculated bond orders and group charges for $[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^-$ and $C_2B_{10}H_{12}$ are listed in Table 5.

**Table 5**. Calculated data for the icosahedral (bicapped pentagonal antiprismatic) *closo*-cluster systems $[B_{12}H_{12}]^{2-}$, $[1\text{-}CB_{11}H_{12}]^-$ and 1,12-$C_2B_{10}H_{12}$.

(a) Bond distances / pm (bond orders in parentheses)

| System | $C_{a_1}B_{t_1}$ | $B_{t_1}B_{t_1}$ | $B_{t_1}B_{t_2}$ | $B_{t_2}B_{t_2}$ | $B_{a_2}B_{t_2}$ |
|---|---|---|---|---|---|
| $[B_{12}H_{12}]^{2-}$ | - | 178 (0.54) | 178 (0.54) | 178 (0.54) | 178 (0.54) |
| $[1\text{-}CB_{11}H_{12}]^-$ | 170 (0.57) | 178 (0.44) | 177 (0.54) | 178 (0.53) | 178 (0.53) |
| 1,12-$C_2B_{10}H_{12}$ | 170 (0.57) | 178 (0.43) | 177 (0.54) | 178 (0.43) | - |

(b) Group charges (total order of skeletal bonds to that group)

| System | $C_{a_1}H$ | $B_{t_1}H$ | $B_{t_2}H$ | $B_{a_2}H$ |
|---|---|---|---|---|
| $[B_{12}H_{12}]^{2-}$ | - | -0.17 (2.70) | -0.17 (2.70) | -0.17 (2.70) |
| $[1\text{-}CB_{11}H_{12}]^-$ | -0.43 (2.85) | +0.04 (2.53) | -0.14 (2.67) | -0.10 (2.65) |

| | | | | |
|---|---|---|---|---|
| 1,12-$C_2B_{10}H_{12}$ | -0.38 (2.85) | +0.07 (2.51) | +0.07 (2.51) | - |

The introduction of a CH unit to replace one of the $BH^-$ units of $[B_{12}H_{12}]^{2-}$, as in the case of the earlier mono-carba anions we have been considering, generates a species $[CB_{11}H_{12}]^-$ in which the CH unit bears a charge (-0.43 a.u.) larger than that (0.17 a.u.) borne by the BH unit it replaces, and depletes the charge on each of the BH units in the adjacent tropical sites to such an extent that they acquire a small positive charge (+0.05 a.u.). The more remote tropical BH units suffer less charge depletion than the antipodal BH unit (antipodal effects are a familiar feature of icosahedral carborane chemistry).[50] The bond order of each of the five BC bonds (0.57) is higher than that of the BB bonds replaced (0.54). The BB bonds more remote from the carbon atom have bond orders only marginally reduced from the calculated values in the parent dianion.

Introduction of a second carbon atom in the site opposite to the first, to form *para*-carborane 1,12-$C_2B_{10}H_{12}$, generates a species which, like 1,10-$C_2B_8H_{10}$, contains only one type of CH unit and one type of BH unit, one type of BC link and two types of BB link (within each tropic and between tropics). The CH units acquire significant negative charges (-0.35 a.u.), leaving each of the BH units with a small positive charge (+0.07 a.u.). The BC skeletal links are those with the highest calculated bond order (0.57) in their skeletons. The BB links within the tropics are calculated to have bond orders significantly lower than those between tropics (Table 5), though their lengths remain essentially the same as those in the parent borane dianion.

**The sizes and shapes of these *closo* clusters**

In our discussion so far, and in Tables 1-5, we have focussed on the BB and BC interactions between adjacent atoms in the skeletons of these *closo* borane and carborane clusters. Here, we discuss briefly how their overall sizes and shapes vary on introducing axial CH units into borane clusters. We do so by considering the distances of the skeletal atoms from the centres of the polyhedra, and selected cross-polyhedral distances.

It is usual to discuss borane/carborane clusters as having their skeletal boron and carbon atoms in pseudo-spherical array,[4-7] but only in the case of two of the systems discussed here, viz. $[B_6H_6]^{2-}$ and $[B_{12}H_{12}]^{2-}$, are all of the skeletal atoms on a spherical surface. In the case of $[B_5H_5]^{2-}$ and $[B_{10}H_{10}]^{2-}$ (Fig. 1), the axial boron atoms occupy sites of lower skeletal connectivity than the others, and project **outside** the sphere on which the remaining atoms lie. These clusters can be seen as ellipsoidal rather than spherical. In the case of $[B_7H_7]^{2-}$ , the more highly-connected axial atoms lie closer to the cluster centre than the equatorial atoms, generating an overall toroidal shape. Replacement of [BH] units by $[CH]^+$ units in these clusters causes further shape perturbations that are best illustrated by the data in Table 6, in which we list cluster heights and widths. We define cluster height as the distance along the vertical axis between the axial atoms, which will be either boron or carbon. We define cluster width as twice the horizontal distance of the equatorial or tropical boron atoms from the vertical axis.

The data in Table 6 (first column) reveal the generalisations about the shapes of the boron clusters as a function of the axial atom connectivities already mentioned, the ellipsoidal shapes of $[B_5H_5]^{2-}$ and $[B_{10}H_{10}]^{2-}$ being evident from the greater height than width of these systems, and the toroidal shape of $[B_7H_7]^{2-}$ from the relatively lesser height of this system. When one and then two CH units are introduced into these systems, the dimensions change as shown by the entries in the second and third columns in Table 6. As BC bonds in these systems are some 8-12 pm shorter than the BB distances in the parent borane, because carbon atoms are smaller than boron atoms, the carbon atoms in the carborane systems end up nearer to the cluster centre than the boron atoms they replace. The carboranes 1,6-$C_2B_4H_6$ and 1,12-$C_2B_{10}H_{12}$ are toroidal, effectively squashed from spherical by compression along the C....C axis. Similar compression along the C...C axis makes 1,5-$C_2B_3H_5$ and 1,10-$C_2B_8H_{10}$ more nearly spherical than the parent boranes, whereas 1,7-$C_2B_5H_7$ is even more compressed from spherical along the 1,7- axis than the parent borane $[B_7H_7]^{2-}$. Cross-polyhedral BB, BC and CC bond orders have been calculated for all interactions between atoms on opposite sides of all of the *closo*-boranes and carboranes we have been discussing. Such cross-polyhedral interactions have been found to be very weak, with bond orders of < 0.11. The bond order values for an illustrative set of such interactions, along the vertical axes of the polyhedra, are listed in Table 7, from which it can be seen that, only in the case of the 6- and 7-vertex clusters do these cross-polyhedral interactions become significant, for the structural reasons just discussed.

Table 6. Heights (h) and widths (w) of clusters

| n | $[B_nH_n]^{2-}$ | $[CB_{(n-1)}H_n]^-$ | $C_2B_{(n-2)}H_n$ |
|---|---|---|---|
| | h (w) pm | h (w) pm | h (w) pm |
| 5 | 261 (209) | 244 (210) | 226 (213) |
| 6 | 245 (245) | 230 (243) | 216 (242) |
| 7 | 231 (282) | 221 (279) | 210 (277) |
| 10 | 373 (259) | 354 (260 $t_1$, 260 $t_2$) | 336 (261) |
| 12 | 339 (303) | 322 (302 $t_1$, 304 $t_2$) | 305 (303) |

Table 7. The calculated weak cross polyhedral BB, BC and CC bond orders along the 'height' axis of the *closo*-boranes $[B_nH_n]^{2-}$, [1-$CB_{n-1}H_n]^-$ and 1,n-$C_2B_{n-2}H_n$.

| n | $[B_nH_n]^{2-}$ | $[CB_{(n-1)}H_n]^-$ | $C_2B_{(n-2)}H_n$ |
|---|---|---|---|
| | BB bond order | BC bond order | CC bond order |
| 5 | 0.07 | 0.06 | 0.06 |
| 6 | 0.09 | 0.09 | 0.11 |
| 7 | 0.09 | 0.11 | 0.15 |
| 10 | 0.06 | 0.05 | 0.04 |
| 12 | 0.03 | 0.03 | 0.02 |

In assessing the significance of the widths of the 10- and 12-atom clusters in Table 6, it should be borne in mind that these are tropical widths, not equatorial widths. The

antiprismatic $B_8H_8$ and $B_{10}H_{10}$ cores of these systems in fact show remarkably little change in shape and size as the axial BH units are replaced by CH units. In the 10-atom systems, the distances of the tropical boron atoms from the cluster centre remain at 150 pm throughout, and in the 12-atom systems at 169 pm, not significantly affected by whether BH or CH units occupy the axial sites.

## Conclusions

Our calculations allow the following generalisations to be made about the bonding and charge distribution in the selected carboranes, in which carbon atoms occupy pyramidal (axial) sites, bonded to sets of three, four or five boron atoms in clusters with overall bipyramidal or bicapped antiprismatic geometries. In interpreting the data, it should be borne in mind that, although the charges calculated for each BH or CH unit in a particular cluster add up to the overall charge of -2 for the dianions, -1 for the monocarba-species $[CB_{n-1}H_n]^-$, and zero for the neutral carboranes $C_2B_{n-2}H_n$, the calculated skeletal bond orders throughout all of the cluster systems we have considered here add up to totals that exceed the numbers of skeletal bond pairs formally available.

The calculated bond orders and interatomic distances in the title compounds show the familiar broad trends towards longer bonds and lower bond orders as the cluster size and atom connectivity increase, and as the number of skeletal electron pairs per skeletal atom decreases. Group charges tend to be less negative as skeletal connectivities increase. The bond orders of the axial-equatorial BC bonds in the bipyramidal clusters, and of the axial-tropical BC bonds in the bicapped antiprismatic clusters, are calculated to be only slightly greater than the bond orders of the BB bonds in the parent borane dianion.

In the bipyramidal clusters with 5, 6 or 7 skeletal atoms, the axial CH units generally though not always acquire greater negative charges than those on the axial BH units in the parent borane cluster dianions. Replacing axial BH units by axial CH units depletes electron density from the equatorial BH units and reduces the BB bond order round the equator, though this is not always evident from the calculated bond distances.

In the bicapped antiprismatic clusters, similar trends are found, the axial CH units acquiring greater negative charges than those borne by the corresponding BH units in the parent borane dianion, depleting charge from the adjacent tropical BH units, and reducing the orders of the bonds between them. The orders of the axial-tropical BC bonds are a little greater than the orders of the comparable axial-tropical BB bonds in the parent anionic borane. The orders of the bonds between the two tropics, however, show no significant change as BH units are replaced by CH units.

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